Assessment of Ra^{226} and Toxic Element Distribution at Tennessee Valley Authority Phosphate Slag Stockpiles, Muscle Shoals, AL

By Alexander May and James R. Boyle, Jr.

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Report of Investigations 9288

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	Mgal/d	million gallon per day
cm	centimeter		
cm/s	centimeter per second	mL	milliliter
ft	foot	pCi/g	picocurie per gram
in	inch	pct	percent
in/h	inch per hour	ppm	part per million
in/yr	inch per year		
m	meter	s	second

ASSESSMENT OF RA^{226} AND TOXIC ELEMENT DISTRIBUTION AT TENNESSEE VALLEY AUTHORITY PHOSPHATE SLAG STOCKPILES, MUSCLE SHOALS, AL

By Alexander May[1] and James R. Boyle, Jr.[2]

ABSTRACT

The U.S. Bureau of Mines conducted studies to determine if phosphate slag stockpiles at Tennessee Valley Authority's National Fertilizer Development Center were hazardous materials. The stockpiles were not hazardous materials as determined by Environmental Protection Agency (EPA) extraction procedure (EP) toxicity test. Radium-226 concentration was 28.7 pCi/g in slag and 2.1 pCi/g in background material. Radium-226 was not leached from the slag. Fluoride concentration was 3.87 pct in slag, 0.18 pct in subsurface material under slag, and 0.08 pct in the background. Slag material permeability was 1.65×10^{-3} cm/s, and subsurface material permeability was 3.24×10^{-6} cm/s. Rain water, trapped in a depression on top of the east slag stockpile, became seepage water at the base of the stockpile. Concentrations of EPA toxic elements in seepage water were much less than concentrations from an EPA EP toxicity test on the slag. Twelve elements—Na, Mg, Ca, Sr, Ba, Cr, Mn, Co, Cu, Cd, Al, and P—had higher concentrations in seepage water than in rain water on top of the slag stockpiles, or in creek water adjacent to stockpile bases, indicating that they were leached from slag stockpiles.

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INTRODUCTION

The mission of the U.S. Bureau of Mines is to assure the Nation of adequate supplies of minerals necessary to maintain national security and for domestic needs. The Bureau also seeks to provide technological advances to reduce undesirable environmental effects of producing, using, reusing, and disposing mineral wastes. One of the research projects at the Bureau's Tuscaloosa Research Center (TURC), Tuscaloosa, AL, is to determine the extent and composition of waste materials, as well as environmental effects of these materials.

Tennessee Valley Authority's (TVA) National Fertilizer Development Center (NFDC) at Muscle Shoals, AL, has a phosphate slag landfill containing approximately 1,640,000 tons of waste slag, located adjacent to the Tennessee River. This slag is primarily calcium silicate ($CaSiO_3$), but is referred to as phosphate slag because it is the major byproduct of elemental phosphorus production. White phosphorus was produced by the electric arc process (1),[3] in which phosphate ore, silica (SiO_2), and coke were fused in an electric furnace at temperatures between 1,200° and 1,500° C, and elemental phosphorus was distilled off. An initial reaction, illustrated by reaction A, involves defluorination of the phosphate ore, represented by its major phosphate mineral, fluorapatite. Reaction A could be divided by 2 and still be balanced, but it is expressed as shown because reactions A through D are balanced together.

On further heating, the apatite structure in hydroxyapatite disintegrates, yielding tricalcium phosphate [$Ca_3(PO_4)_2$] (reaction B).

The $Ca_3(PO_4)_2$ heated with SiO_2 and coke yields elemental phosphorus, which is distilled off (reaction C).

The HF (reaction A) reacts with the CaO (reaction B) to yield CaF_2 (reaction D).

The slag consists primarily of $CaSiO_3$ (reaction C) and CaF_2 (reaction D), in a mole ratio of 9 to 1, silicate to fluoride. However, HF may also react with SiO_2 to produce volatile SiF_4; impurities are present in the phosphate ore; and other reactions occur, so the slag contains minor amounts of compounds of Fe, Al, Mg, and other elements.

Production of elemental phosphorus, and slag, began in 1934 and continued until 1976. Initially, the slag was placed in the landfill, and later, some of the slag was granulated and sold for use as an agricultural liming agent, soil conditioner, construction material, and fill material for rail and roadbeds. Beginning in 1947, NFDC produced more slag than it could market, and a system was installed to transport the slag to the landfill. NFDC halted all sales of slag in December 1978 because of a question of radioactivity. In 1987, the Bureau approached NFDC, asking to use the TVA slag piles as part of a project study. The timing dovetailed well with the potential sale of slag, and NFDC agreed readily to the evaluation of the TVA site.

In 1982, the Bureau assessed the environmental impacts associated with phosphogypsum in Florida (2). An inventory of the stockpiles in Florida was made, and the material was characterized, including its radioactivity. In 1983, the Bureau evaluated the Ra^{226} and toxic element leaching characteristics of these stockpiles (3). These investigations were nearly identical to that needed by NFDC. Because of the Bureau's experience in environmental assessments of phosphate-related wastesites, and continuing cooperation between TVA and the Bureau, the Bureau undertook this investigation of the phosphate slag stockpiles.

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[3]Italic numbers in parentheses refer to items in the list of references preceding the appendixes at the end of this report.
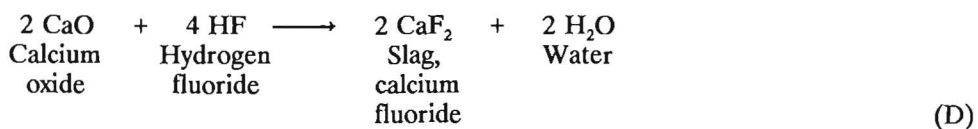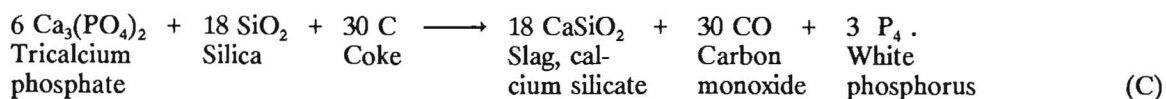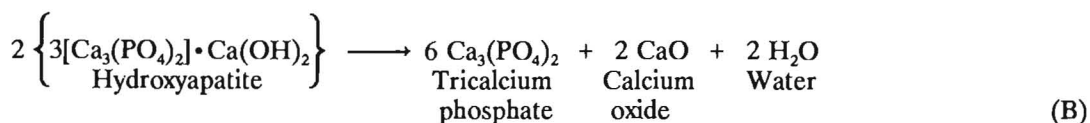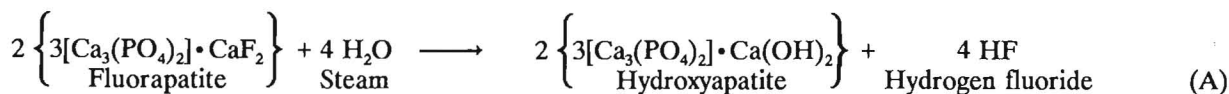
$$2 \left\{ \begin{array}{c} 3[Ca_3(PO_4)_2] \cdot CaF_2 \\ \text{Fluorapatite} \end{array} \right\} + \underset{\text{Steam}}{4\ H_2O} \longrightarrow 2 \left\{ \begin{array}{c} 3[Ca_3(PO_4)_2] \cdot Ca(OH)_2 \\ \text{Hydroxyapatite} \end{array} \right\} + \underset{\text{Hydrogen fluoride}}{4\ HF} \qquad (A)$$

$$2 \left\{ \begin{array}{c} 3[Ca_3(PO_4)_2] \cdot Ca(OH)_2 \\ \text{Hydroxyapatite} \end{array} \right\} \longrightarrow \underset{\substack{\text{Tricalcium} \\ \text{phosphate}}}{6\ Ca_3(PO_4)_2} + \underset{\substack{\text{Calcium} \\ \text{oxide}}}{2\ CaO} + \underset{\text{Water}}{2\ H_2O} \qquad (B)$$

$$\underset{\substack{\text{Tricalcium} \\ \text{phosphate}}}{6\ Ca_3(PO_4)_2} + \underset{\text{Silica}}{18\ SiO_2} + \underset{\text{Coke}}{30\ C} \longrightarrow \underset{\substack{\text{Slag, cal-} \\ \text{cium silicate}}}{18\ CaSiO_3} + \underset{\substack{\text{Carbon} \\ \text{monoxide}}}{30\ CO} + \underset{\substack{\text{White} \\ \text{phosphorus}}}{3\ P_4} \qquad (C)$$

$$\underset{\substack{\text{Calcium} \\ \text{oxide}}}{2\ CaO} + \underset{\substack{\text{Hydrogen} \\ \text{fluoride}}}{4\ HF} \longrightarrow \underset{\substack{\text{Slag,} \\ \text{calcium} \\ \text{fluoride}}}{2\ CaF_2} + \underset{\text{Water}}{2\ H_2O} \qquad (D)$$

ACKNOWLEDGMENTS

DESCRIPTION OF PHOSPHATE SLAG SITE

PHOSPHATE SLAG STOCKPILE

TVA's NFDC is in Colbert County, in the northwest corner of Alabama (fig. 1). The slag stockpile is in the northernmost edge of the property on the Tennessee River. Figure 2 shows an aerial view of the phosphate slag stockpile. The site is split into east and west sections by an unimproved road. The east stockpile has approximately 1 million tons of slag and is a rough rectangle. The east-west leg is approximately 1,300 ft; the north-south, approximately 1,500 ft. The east border is Pond Creek, which flows into the Tennessee River. There is approximately 1,500 ft of forested buffer zone between this stockpile and the Tennessee River. The west stockpile has approximately 640,000 tons of slag and is irregular in shape. It is approximately 2,000 ft long by 1,000 ft wide, extending to the Tennessee River. The aerial view shows eight circular depressions (fig. 2). These depressions served as holding ponds for plant effluent. The effluent was allowed to seep into the stack, with $CaSiO_3$ acting as a buffer. All but one of the ponds has long since dried up. The one pond still holding water was sampled.
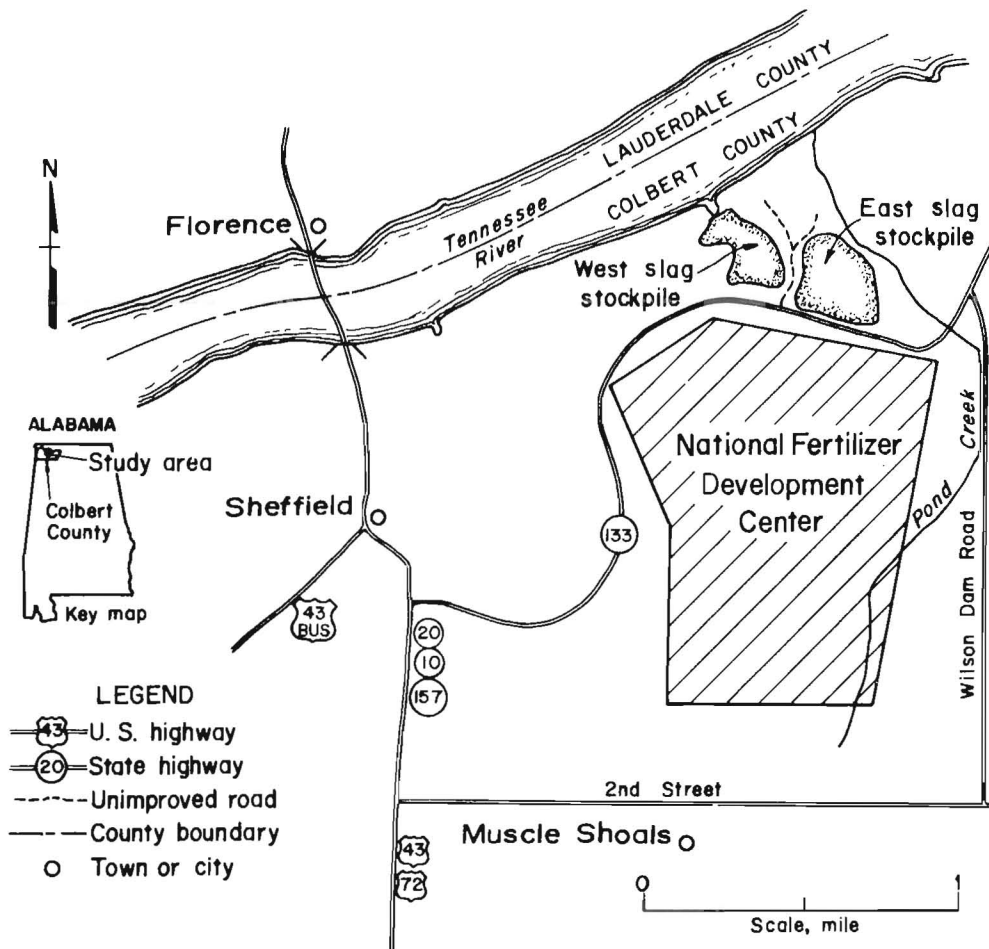
Figure 1.–Area map.

Figure 2.–Aerial view of slag stockpile site.

GEOLOGY AND HYDROLOGY OF STUDY SITE

Information from the Geological Survey of Alabama (4) shows that the area of the study site is underlain by a regolith, limestone, and cherty limestone. Figure 3 shows a typical core section. The regolith is an unstratified clay with chert fragments. The clay is from 20 to 60 ft thick. The regolith's contribution to the water supply is limited to dug or drilled shallow wells that are for domestic use (4).

Tuscumbia Limestone underlies the regolith. This limestone formation is approximately 40 ft thick. The limestone is gray, medium bedded, and very hard. It is a productive aquifer where the ground water occurs in solution openings along bedding and fracture planes (5). Underlying the limestone is the Fort Payne Chert. This is also a limestone formation, but it contains large quantities of chert. It is approximately 180 ft thick. Like the Tuscumbia Limestone, the Fort Payne Chert is a good aquifer where ground water occurs in solution openings along fracture and bedding planes (5).

The average annual precipitation for the study area is 51 in/yr. March has the highest monthly rainfall at 5.7 in, while September has the lowest at 2.9 in. The movement of ground water in the area and at the site is in a west-northwest direction (5), as shown by the piezometric map in figure 4. This map shows the water pressure surface by plotting and contouring the altitudes of the water levels in various observation wells. The ground water moves from higher to lower altitudes.

The main surface waters of the area are the Tennessee River and Pond Creek. The Tennessee River runs east to west and makes up the north boundary of the site. The Tennessee River has an annual 7-day low flow of greater than 1,000 Mgal/d. Pond Creek makes the east boundary of the site and flows into the Tennessee River. Pond Creek has an annual 7-day low flow of less than 2 Mgal/d (5). There are several small valleys with creeks in the area that discharge into the Tennessee River. These normally have water only after heavy rainfall.
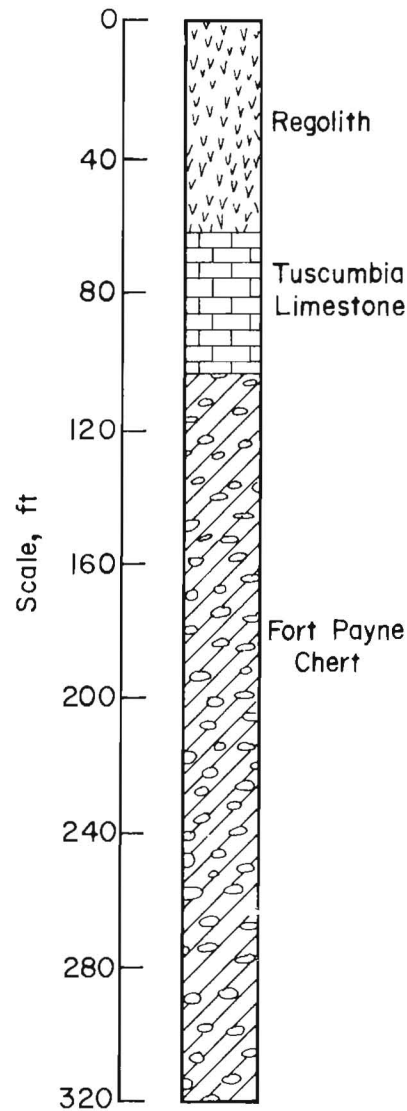
Figure 3.–Typical core-section. (Courtesy Geological Survey of Alabama)
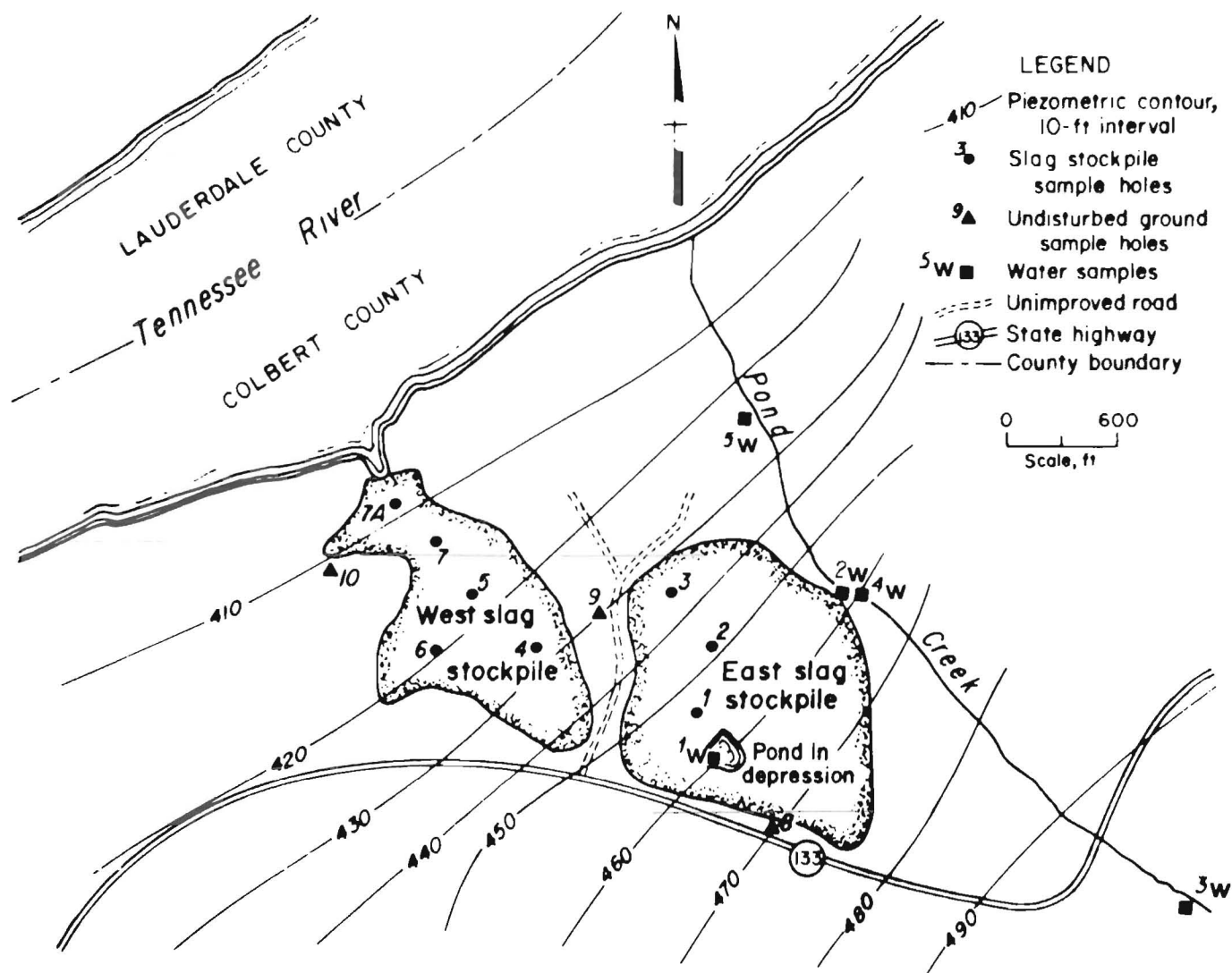
Figure 4.–Piezometric map of slag stockpile site with core and water sample locations.

PROCEDURES

In this report, *slag* refers to the phosphate slag stockpiled material, *subsurface* refers to the material directly under the stockpiles, and *ground* refers to material never covered by the phosphate slag. Cores 1, 2, and 3 were from the east slag stockpile; cores 4, 5, 6, 7, and 7A, from the west stockpile; core 8, the ground east of the stockpiles; core 9, the ground between the stockpiles; and core 10, the ground west of the stockpiles. The depths of each core sample are given in table 1. The elements are listed alphabetically in the tables but, in certain illustrations, they are listed on the X-axis by groups as they occur in the periodic table.

Table 1.–Depth of samples from top of slag stockpiles, or subsurface-slag interface, or ground, feet

Core	Top	Middle	Bottom
EAST STOCKPILE			
Slag:			
1	1-6	15-20	35-40
2	1-4	20-25	45-50
3	1-5	10-15	35-40
Subsurface:			
1	1-5	14-19	25-29
2	0-4	15-19	25-29
3	1-5	15-19	24-29
WEST STOCKPILE			
Slag:			
4	1-5	15-20	35-40
5	1-5	15-20	35-40
6	1-5	10-15	20-25
7	1-5	10-15	20-25
7A	1-5	15-20	30-35
Subsurface:			
4	4-8	NS	NS
5	5-9	NS	NS
6	0-4	15-19	23-24
7	NS	NS	NS
7A	0-9	NS	NS
GROUND			
8	4-8	25-29	45-49
9	1-5	20-24	40-44
10	1-5	10-14	20-24

NS   No sample obtained.

Figure 5.–Split spoon being lowered into hollow-stem auger hole.

SAMPLING PROCEDURE

Samples of slag and the underlying regolith were taken using hollow-stem auger and split-spoon sample retrievers (figs. 5-6). The split spoon was a thin-walled tube, 2 ft long and 2 in. in diameter, which is split in two sections along its length. The tube was driven by a hammer into the material sampled because of the chert in the regolith.

Three holes were drilled and sampled in the east stockpile, four in the west stockpile, and three in undisturbed ground. The sample holes in undisturbed ground were placed in the direction of the ground water movement (fig. 4). An additional hole, 7A, was drilled in the west stockpile because subsurface samples could not be obtained at hole 7 owing to bedrock conditions encountered.

The stockpile sampling procedure was to first drill a pilot hole through the stockpile and into the subsurface to determine the depth of the stockpile so that the middle and bottom sections could be located for sampling. The auger string was removed from the pilot hole and the sample hole was begun next to the pilot hole. The first foot of the sample hole was augered, then the split spoon was used to recover 4 ft of sample. The middle and bottom of the stockpile were sampled in the same way. The hole was continued through the stockpile and into the subsurface regolith. The first 1 to 2 ft of clay was augered and 4 ft of top subsurface was recovered. The middle and bottom of the subsurface were sampled in the same way, normally with 10 to 15 ft between the top and middle subsurface samples and 5 to 10 ft between the middle and bottom subsurface samples, depending upon the drilling conditions. A typical hole yielded three phosphate slag and three subsurface samples, but conditions sometimes limited the number of subsurface samples. The holes drilled in undisturbed ground were sampled using the same procedure used for the subsurface samples. Three samples (top, middle, and bottom) were recovered from each hole drilled in undisturbed ground.

Each of holes 1, 2, and 3 of the east stockpile and hole 6 in the west stockpile had six samples (three slag and three subsurface). Each of holes 4, 5, 7, and 7A in the west stockpile had three slag samples and (except hole 7) one subsurface sample. These holes struck bedrock only 6 ft below the surface of the stockpile. Hole 7 in the west stockpile had three slag samples but no subsurface samples because bedrock was hit immediately below the stockpile. Holes 8, 9, and 10 in undisturbed ground had three samples each.

The slag, subsurface, and undisturbed ground samples were placed in plastic bags and sealed for transport back to TURC. The subsurface and undisturbed ground samples were all a red, moist cherty clay, typical of the regolith in the area. Figure 6 shows split spoons of clay samples.

Figure 6.--Split-spoon samples.

Five surface water samples--three from Pond Creek, one from the pond formed in the east stack depression, and one from a seep coming off the east stack and flowing into Pond Creek--were collected. The creek samples were taken upstream and downstream of the east stack and at the toe of the stack. During field reconnaissance in the spring of 1987, the seep and depression pond were found. When drilling began in the summer of 1987, the seep still flowed and water was still in the depression, so samples were collected from both. Figure 4 shows the sample hole locations and the locations where the water samples were collected.

The water samples were collected in 500-mL plastic containers. Temperature and pH were taken at the time of sampling. The core samples and water samples were taken to TURC, prepared, split into representative samples and composites, and sent to the Bureau's Reno Research Center and the Oak Ridge National Laboratory for analysis. The water samples and composites were designated as shown in table 2.

Table 2.--Sample Identifications

Water:

1W	...	Depression pond in east slag stockpile.
2W	...	Seepage from east slag stockpile.
3W	...	Pond Creek, upstream from east slag stockpile.
4W	...	Pond Creek, at east slag stockpile.
5W	...	Pond Creek, downstream from east slag stockpile.
6W	...	West Creek, dry-no sample.

Composite:

1C	...	East slag pile, middle samples, cores 1-3.
2C	...	West slag pile, middle samples, cores 4-7A.
3C	...	Ground, middle samples, cores 8-10.
4C	...	East slag pile, subsurface, top samples, cores 1-3.
5C	...	West slag pile, subsurface, top samples, cores 4-7A.

PERMEABILITY AND ANALYTICAL METHODS

The standard variable head method (6) was used to determine the permeability to the flow of water of the phosphate slag material and of the subsurface material. Methodology used for treatment of permeability data is presented in appendix B. Glass columns, 7/8 in. in diameter, were packed with each material, and the flow of water versus time was measured. Although the laboratory method suffered from the disadvantages as discussed in references 6 and 7, such as use of small-diameter columns and disturbed samples, the results gave a good comparison of the permeability of the slag with that of the subsurface material.

The following analytical methods were employed in this investigation:

1. Inductively coupled plasma (ICP) spectrographic "whole rock" analyses. Sample preparation by lithium metaborate fusion and/or acid digestion.
2. Mineralogy, X-ray diffraction analyses.
3. Atomic absorption analyses.
4. Radiometric analyses for Ra^{226}.
5. Toxic elements by EPA EP toxicity test.
6. Electrometric analyses for pH and ion-selective electrode for fluoride.
7. Gravimetric analyses for Si and moisture.

Moisture contents and spectrographic analyses are given in appendix A.

TEST RESULTS

MINERALOGY

The mineralogical analyses by X-ray diffraction of the composite samples showed that the slag samples, 1C and 2C, were amorphous and no minerals were identified. The major mineral detected in the ground sample, 3C, was quartz, with a minor amount of kaolinite and a trace amount of hematite.

CHEMICAL ANALYSES–MAJOR COMPONENTS

The moisture contents of the core samples are given in table A-1 in appendix A. The analyses of the major components of the slag and ground composite samples are given in table 3.

Table 3.–Chemical analyses of major components of slag and ground composite samples, percent

Constituent	1C	2C	3C	Constituent	1C	2C	3C
Al_2O_3	7.2	7.4	10.8	MnO	0.1	0.1	0.1
CaO	44.5	44.6	.3	Na_2O	.4	.4	.1
F	4.2	3.9	.1	P	.9	.6	.1
Fe_2O_3	1.9	1.4	4.7	SiO_2	44.1	46.4	83.9
K_2O	.3	.3	.3	Sum	104.5	105.6	100.5
MgO	.5	.5	.3				

1C East slag pile, middle samples, cores 1-3.
2C West slag pile, middle samples, cores 4-7A.
3C Ground, middle samples, cores 8-10.

PERMEABILITY

Permeability was determined by measuring the times and levels of water flowing through samples of slag and subsurface material (6). Water flowed freely through the slag and almost not at all through the subsurface material. The data are given in table 4. The permeability of the slag material was 1.65×10^{-3} cm/s (2.34 in/h), and the permeability of the subsurface material was 3.24×10^{-6} cm/s (4.59×10^{-3} in/h).

Table 4.–Permeability data for water seepage through slag and subsurface material

Slag		Subsurface	
Time (t), s	Water height[1] (h), cm	Time (t), s	Water height[1] (h), cm
0	44.5	0	45.0
1,800	38.4	78,480	44.2
3,960	32.8	165,240	43.7
5,400	30.2	255,960	43.2
7,380	26.4	515,880	41.9

[1]Height of water from bottom of column.

NOTE.–Length (L) of water path column–slag, 23.6 cm; subsurface material, 24.6 cm.

SPECTROGRAPHIC ANALYSES

ICP spectrographic analyses were performed on 24 slag samples, 15 subsurface samples, 9 ground samples, and 5 water samples; each sample was analyzed for 32 elements, for a total of 1,696 analyses. Table A-2 summarizes the average concentrations of the elements in the slag, subsurface, and ground samples and their standard deviations. Table A-3 gives the average concentrations of elements in the east and west slag stockpiles; in the top, middle, and bottom slag samples; and their standard deviations. Table A-4 gives the average concentrations of elements in the top ground samples, and table A-5 gives the analyses of the water samples.

FLUORIDE, RADIUM-226, AND WATER ANALYSES

Fluoride analyses were run on all slag, subsurface, and ground samples. The analyses are reported in table 5.

Radium-226 analyses were run on the bottom slag samples and the top subsurface and ground samples. The bottom slag and the top subsurface represent the interface between the stacks and the subsurface. The analyses are reported in table 6.

Water analyses were run on samples from the pond at the east stack, seepage from the east stack, and samples from Pond Creek. Analyses for EPA toxic elements and some anions are shown in table 7, which also includes primary drinking water standards (8). Spectrographic metal analyses are given in table A-5.

Table 5.–Fluoride analyses, percent

Core	Top	Middle	Bottom
EAST STOCKPILE			
Slag:			
1	3.4	4.2	4.6
2	3.9	4.2	4.1
3	3.8	4.3	4.7
Subsurface:			
1	.16	.29	.18
2	.17	.14	.11
3	.06	.09	.14
WEST STOCKPILE			
Slag:			
4	4.0	3.5	3.2
5	3.7	3.7	3.9
6	3.6	3.7	3.8
7	3.6	3.8	3.6
7A	4.9	3.6	3.8
Subsurface:			
4	.11	NS	NS
5	.16	NS	NS
6	.14	.16	.73
7	NS	NS	NS
7A	.14	NS	NS
GROUND			
8	0.09	0.07	0.08
9	.08	.05	.12
10	.13	.08	.04

NS   No sample obtained.

Table 6.–Radium-226 analyses, picocuries per gram

Core	Analyses	Std dev
EAST STOCKPILE		
Slag:[1]		
1	23.76	1.91
2	37.74	3.09
3	24.93	2.03
Subsurface:[2]		
1	2.03	.17
2	1.37	.14
3	.86	.08
WEST STOCKPILE		
Slag:[1]		
4	27.13	2.18
5	32.17	2.70
6	31.42	2.59
7A	23.57	1.91
Subsurface:[2]		
4	2.78	.22
5	2.82	.23
6	2.90	.25
GROUND[3]		
8	1.56	0.16
9	1.66	.19
10	2.43	.21

[1]Sample from bottom of stockpile.
[2]Sample from top of subsurface.
[3]Top ground samples.

Table 7.–Water analyses, parts per million

	1W	2W	3W	4W	5W	S
Ag	<0.050	<0.050	<0.050	<0.050	<0.050	0.05
As	<.005	<.005	<.005	<.005	<.005	.05
Ba	<.010	.170	.020	.030	.040	1
Cd	<.004	.010	<.004	<.004	<.004	.010
Cr	<.040	[1].060	<.040	<.040	<.040	.05
Hg	[1].004	[1].006	.001	[1].004	.001	.002
Pb	<.010	.010	<.010	<.010	<.010	.05
Se	.001	.001	<.001	<.001	<.001	.01
Bicarbonate, as $CaCO_3$	8	0	139	100	62	NAp
Carbonate, as $CaCO_3$	0	0	0	0	7	NAp
Chloride	1	1	47	35	33	NAp
Fluoride	[1]31	[1]11	1	1	1	4.0
Hardness, as $CaCO_3$	93	430	74	78	130	NAp
Sulfate	13	45	13	27	25	NAp
pH	6.2	3.7	8.0	8.3	9.1	NAp

NAp   Not applicable.
1W   Depression pond in east slag stockpile.
2W   Seepage from east slag stockpile.
3W   Pond Creek, upstream from east slag stockpile.
4W   Pond Creek, at east slag stockpile.
5W   Pond Creek, downstream from east slag stockpile.
S   Primary drinking water standards (8). For noncompliance with these standards, the maximum contaminant levels must be exceeded, rounded to the digits indicated.
[1]Noncompliance with primary drinking water standards.

EPA EXTRACTION PROCEDURE TOXICITY TESTS

The EPA EP toxicity test was performed on the composite samples in accordance with the standard EPA procedure (9). The results are given in table 8. Reference 9 gives the details of the EP toxicity test, reference 10 lists the EPA toxic elements, and reference 11 gives the details of analytical methods.

Table 8.–EPA EP toxicity test, parts per million

	1C	2C	3C	4C	5C	S
Ag	<1	<1	<1	<1	<1	5.0
As	<.01	<.01	<.01	<.01	<.01	5.0
Ba	17	23	4.0	4.6	5.2	100
Cd	<.07	<.08	<.06	<.08	<.08	1.0
Cr	<.07	<.8	<.6	<.8	<.8	5.0
Hg	.058	.010	.010	.04	.024	.2
Pb	<2	<2	<2	<2	<2	5.0
Se	.021	.021	<.010	.014	<.010	1.0

1C   East slag pile, middle samples, cores 1-3.
2C   West slag pile, middle samples, cores 4-7A.
3C   Ground, middle samples, cores 8-10.
4C   East slag pile, subsurface, top samples, cores 1-3.
5C   West slag pile, subsurface, top samples, cores 4-7A.
S   Maximum concentration of contaminants for characteristic of EPA toxicity (10).

DISCUSSION

MINERALOGY

No minerals were identified in the slag samples by X-ray diffraction, even though reactions C and D indicated that the slag was composed of $CaSiO_3$ and CaF_2. The slag was produced as a melt at 1,200 to 1,500° C, and an amorphous material resulted, which did not diffract X-rays. The mineralogy indicated by the X-ray diffraction for the subsurface material indicated kaolinite and quartz.

CHEMICAL ANALYSES–MAJOR COMPONENTS

The analyses in table 3 are expressed as the oxides for the cations and the elements for the anions, a common practice in reporting analytical results. As stated above, X-ray diffraction techniques did not identify any compound in the slags. The results for the slag samples, 1C and 2C (table 3), may be expressed by calculating the SiO_2 as $CaSiO_3$, with the remaining CaO as CaF_2, which results in some F left over in these calculations. Since the slag sample results can be compared with the calculated quantities of $CaSiO_3$ and CaF_2 from reactions C and D, only Ca, Si, and F were considered. The ground sample, 3C, cannot be expressed this way because there is insufficient CaO. It was expressed by calculating F as CaF_2 and the remaining CaO as $CaSiO_3$; and Al as $Al_4(Si_4O_{10})(OH)_4$, kaolinite, and the remaining SiO_2 as SiO_2, quartz, or chert. Results are shown in table 9.

The excellent agreements between the amounts of $CaSiO_3$ calculated from chemical analysis in each slag sample and that calculated from reactions C and D identify the slag as primarily $CaSiO_3$. The ground material was identified as kaolinite and quartz.

Table 9.–Compounds in slag samples, based on Ca, Si, Al, and F analyses, percent

Compound	1C	2C	3C	Calc[1]
CaF_2	5.1	1.9	0.3	7.0
$CaSiO_3$	92.8	94.9	.4	93.0
SiO_2	.0	.0	70.5	.0
F	2.1	3.2	.0	.0
Kaolinite	.0	.0	28.8	.0
Sum	100.0	100.0	100.0	100.0

1C East slag pile, middle samples, cores 1-3.
2C West slag pile, middle samples, cores 4-7A.
3C Ground, middle samples, cores 8-10.
[1]From reactions C and D.

PERMEABILITY

The permeability of the phosphate slag material was 1.65×10^{-3} cm/s. At this rate, it would take 10.7 days for water to flow through 15.2 m of slag, the maximum depth of the slag stockpiles. The permeability of the subsurface material was 3.24×10^{-6} cm/s. At this rate, the flow of water would penetrate only 1.5 cm of subsurface material, in 53 years (from 1934, when the slag was first produced, to 1987). The permeabilities measured were the saturated hydraulic conductivities because the samples were completely immersed in columns of water during the tests. Unsaturated hydraulic conductivities are much less than the saturated ones because of loss of the waterhead; therefore, the time for water to flow through the slag may be several times greater than the 10.7 days, and the penetration of water into the subsurface may be much less than the 1.5 cm calculated. This indicates that water leaching from the slag stockpiles would not, for all practical purposes, penetrate into the subsurface material but would seep out between the slag and the subsurface material into the drainage basin leading to the Tennessee River.

However, other factors may allow some water to penetrate the subsurface. When the ground is initially dry, it will absorb moisture to a depth of a few feet when it rains, after which it becomes cohesive. The subsurface may act in the same manner, although its drying out is protected by the cover of slag. The average moisture content of the slag was 6.4 pct and that of the subsurface material was 21.1 pct (table A-1).

SPECTROGRAPHIC ANALYSES

The following discussion is restricted to the spectrographic analyses of 24 slag samples, 15 subsurface samples, and 9 ground samples, each analyzed for 32 elements. The analyses of the elements F, Ra, Hg, and Se and water analyses are treated in subsequent sections of this report.

The t-test was used to determine if the averages of two sets of data are statistically the same or different (12). A t-test probability of 0.0000 indicated that there is a zero chance that a difference between averages is due to random variations in the data, while a probability of 1.0000 indicates a 100 pct chance that the difference between averages is caused by random variations. The EPA compares the upper limit of the 80 pct two-tailed confidence level of a possible contaminant concentration to the appropriate regulatory threshold limit. Since the regulatory threshold limits are fixed concentrations, with no distributions, the EPA selection is equivalent to a confidence level of 90 pct or a t-test probability of 0.1000. This same probability, 0.1000, was used in this report; probabilities below 0.1000 indicate that real differences exist in concentrations, while those above 0.1000 indicate that statistically the concentrations are the same, with any differences due to chance.

Figure 7 shows the t-test probabilities for comparing element concentrations in the slag versus the subsurface material. Probabilities greater than 0.1000 in figure 7 show that the concentrations of Li, K, Nb, Mo, Cu, As, and Sb are the same in the slag and in the subsurface material. All other elements differ in their concentrations, as would be expected since the slag and the subsurface material are two entirely different materials.
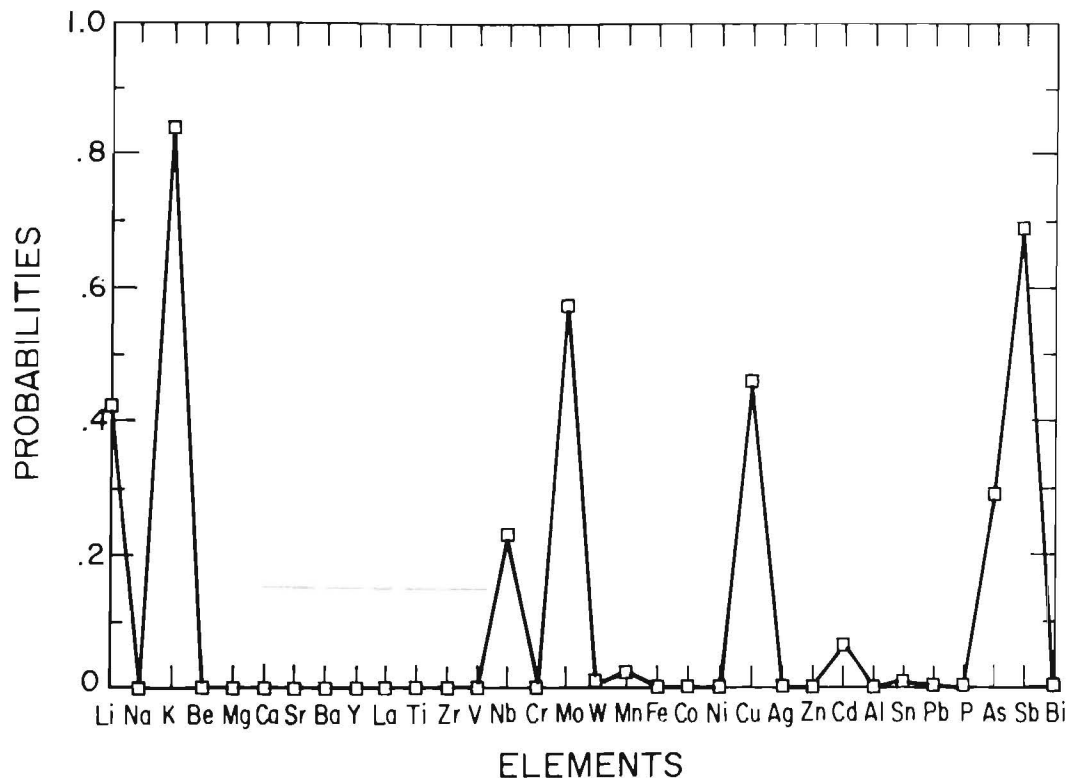
Figure 7.–Slag versus subsurface material t-test probabilities.

Figure 8 shows the t-test probabilities for comparing element concentrations in the subsurface versus the ground material. Probabilities greater than 0.1000 show that the concentrations of 27 elements–Li, Na, K, Mg, Ca, Sr, Ba, Y, La, Zr, V, Nb, Cr, Mo, W, Fe, Ni, Ag, Zn, Cd, Al, Sn, Pb, P, As, Sb, and Bi–are the same in the subsurface as in the ground (fig. 8). The elements that are different in the subsurface and the ground are Be, Ti, Mn, Co, and Cu. The concentrations of Be and Ti are less in the subsurface material than in the ground; thus, the presence of the slag has not increased the concentrations of these elements over that of background. Only Mn, Co, and Cu have concentrations above background, and t-tests probabilities indicate that this may be significant. Thus, of the 32 elements analyzed, only Mn, Co, and Cu may be leached from the slag into the subsurface material to increase their concentrations above background.

Figure 9 shows the t-test probabilities for comparing element concentrations in the east slag stockpile versus the west slag stockpile. The elements Li, Na, Be, Ba, Fe, Al, and Pb had different concentrations in the east and in the west slag stockpiles. The elements Fe and Al had higher concentrations in the west stockpile (table A-3). The east slag stockpile had holding ponds for plant effluent discharge, while the west slag stockpile did not. This could have caused differences in these stockpiles. Differences in concentrations and analyses may also be attributed to the use of two sources of rock. Beneficiated

Tennessee rock was used early in the operation. Later, Tennessee rock without beneficiation and Florida rock were used together and separately in the process.

Figure 10 shows the t-test probabilities for comparing element concentrations in the top slag samples versus the bottom slag samples. The elements Li, Be, Sr, Cr, Mo, Fe, Ni, Cu, Zn, Al, Sn, and Sb had different concentrations in the top samples than in the bottom samples, with Be, Zn, and Sn having higher concentrations in the bottom samples (table A-3).

Concentrations of elements in the top ground samples east, between, and west of the stockpiles are tabulated in table A-4. Only moderate differences in concentrations of the elements are evident, and these differences were approximately within the analytical errors for analysis of the elements.

To illustrate the conclusions reached from the probabilities of the t-tests, graphs for the element concentrations versus cores for Ba, Cr, and As are shown by figures 11, 12, and 13, respectively. Similar graphs can be drawn for each element, but these illustrate the conclusions reached from the probabilities. For Ba (fig. 11), at core 1, a concentration of 550 ppm is the top slag sample Ba concentration, and the concentration of 150 ppm is the top subsurface Ba concentration; the next two data points are from the middle samples and the next two are from the bottom samples. This repeats under core 2, etc. Figure 11 shows that the Ba concentrations in the slag and the

subsurface material are distinctly different, while the concentrations in the subsurface and the ground are essentially the same. This agrees with a subsurface-slag probability of 0.0000 and a subsurface-ground probability of 0.8565. The results for Cr (fig. 12) are similar to those for Ba, while those for As (fig. 13) show that there are no distinct differences among the slag, subsurface, and ground concentrations, agreeing with probabilities of 0.2920 and 0.5429 for the subsurface-slag and subsurface-ground probabilities for As, respectively. The graph for Cr indicated that concentrations in the subsurface material reflect changes in concentrations in the slag. Similar changes were noted in concentrations of As, Cd, and Co. This may indicate some effect of the slag on the subsurface material.
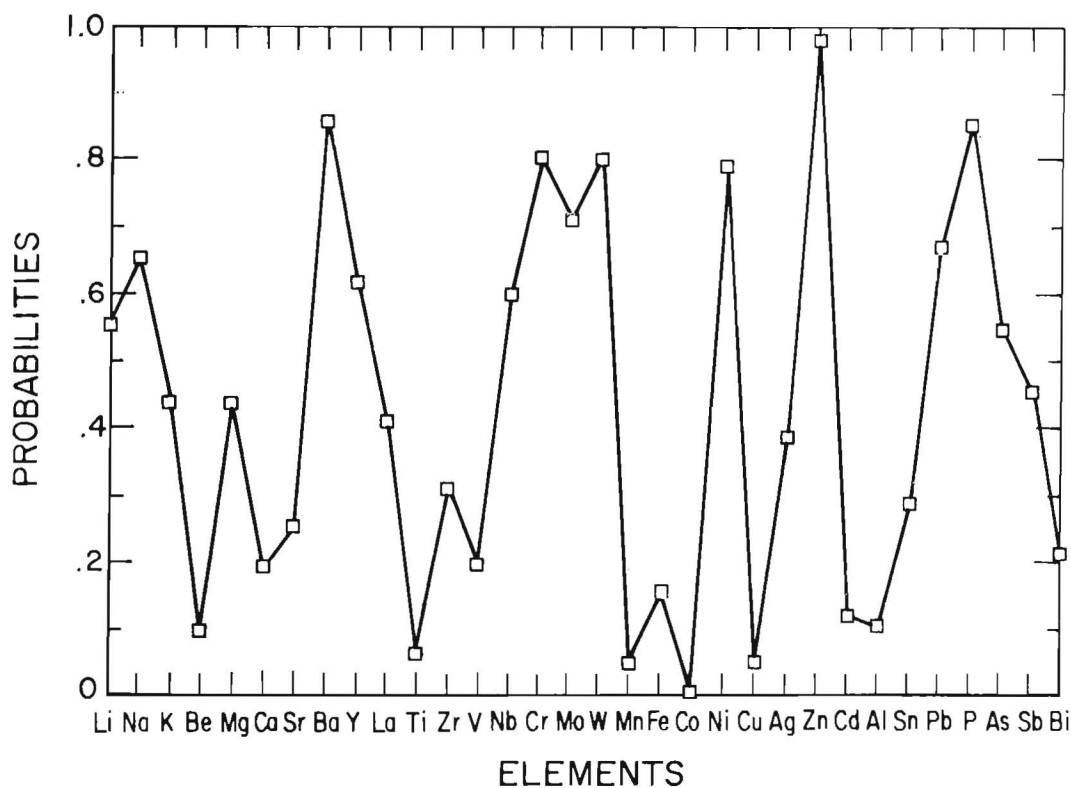
Figure 8.–Subsurface versus ground material t-test probabilities.
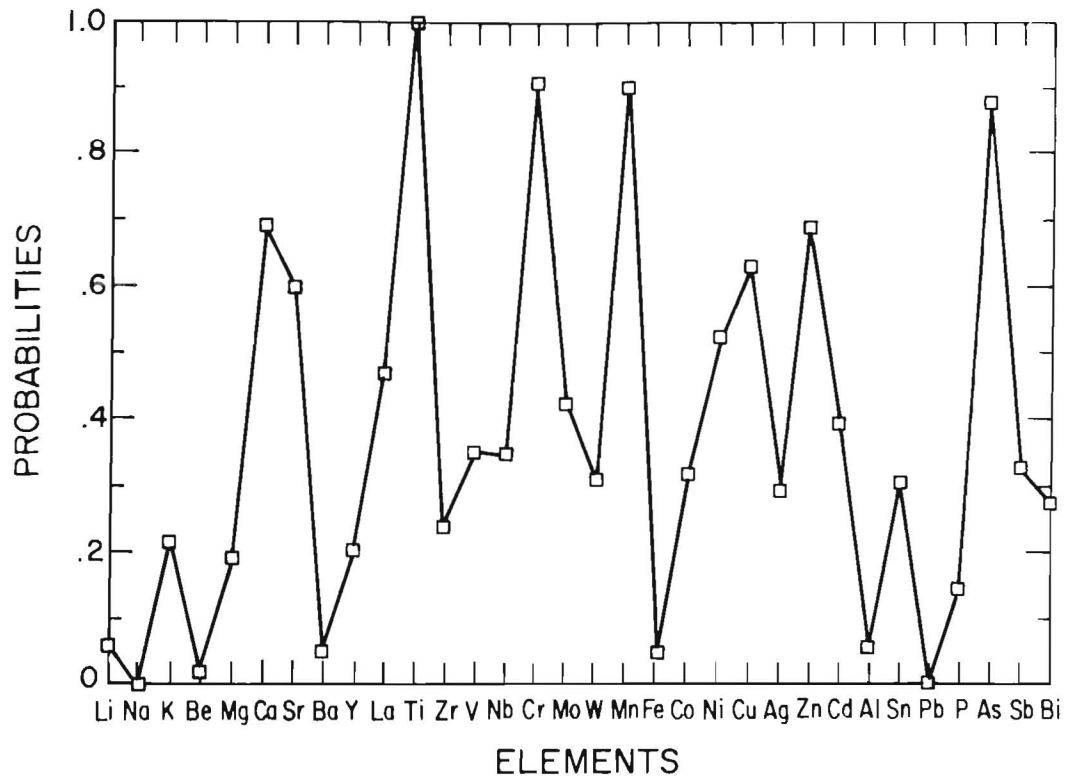
Figure 9.--East versus west slag material t-test probabilities.
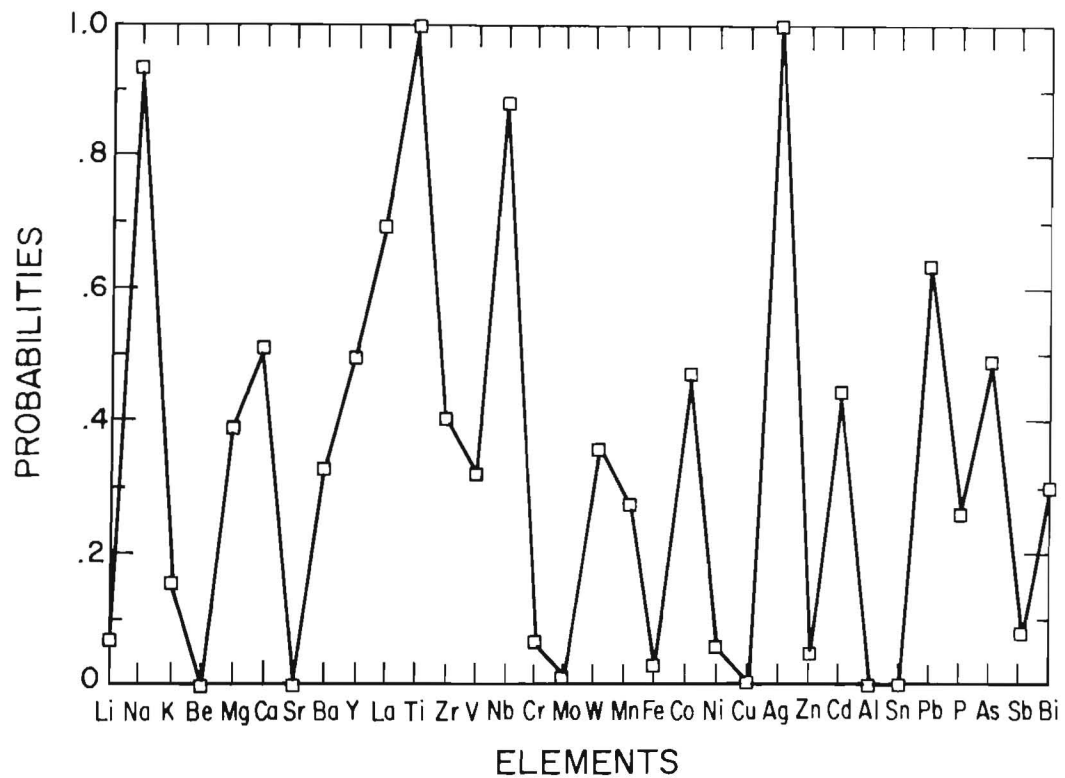
Figure 10.--Top versus bottom slag material t-test probabilities.
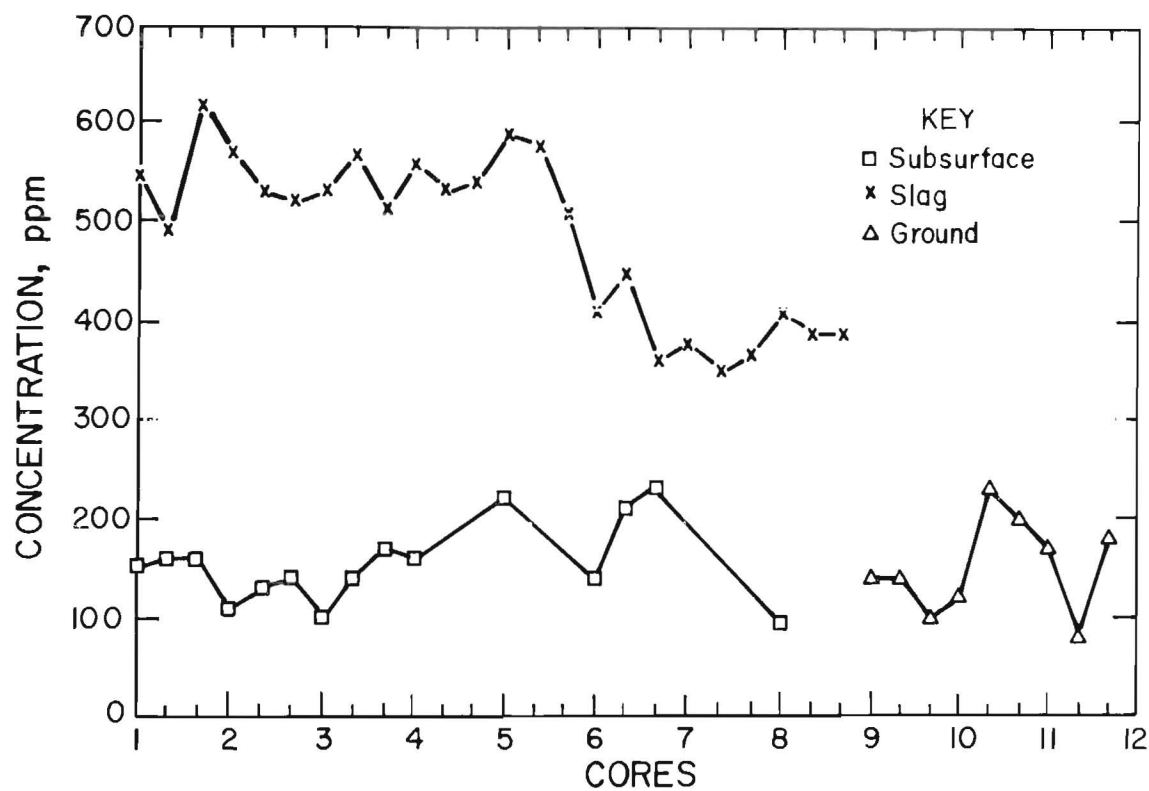
Figure 11.–Barium concentrations in slag, subsurface, and ground material.
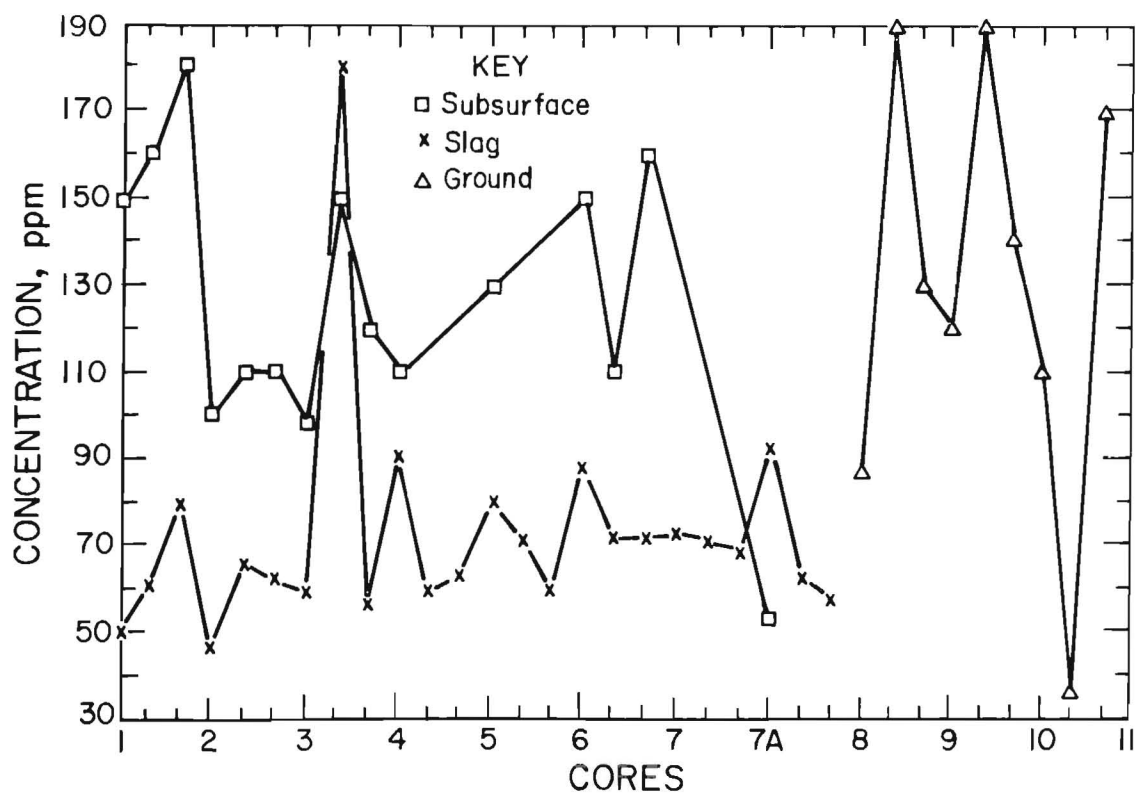
Figure 12.–Chromium concentrations in slag, subsurface, and ground material.
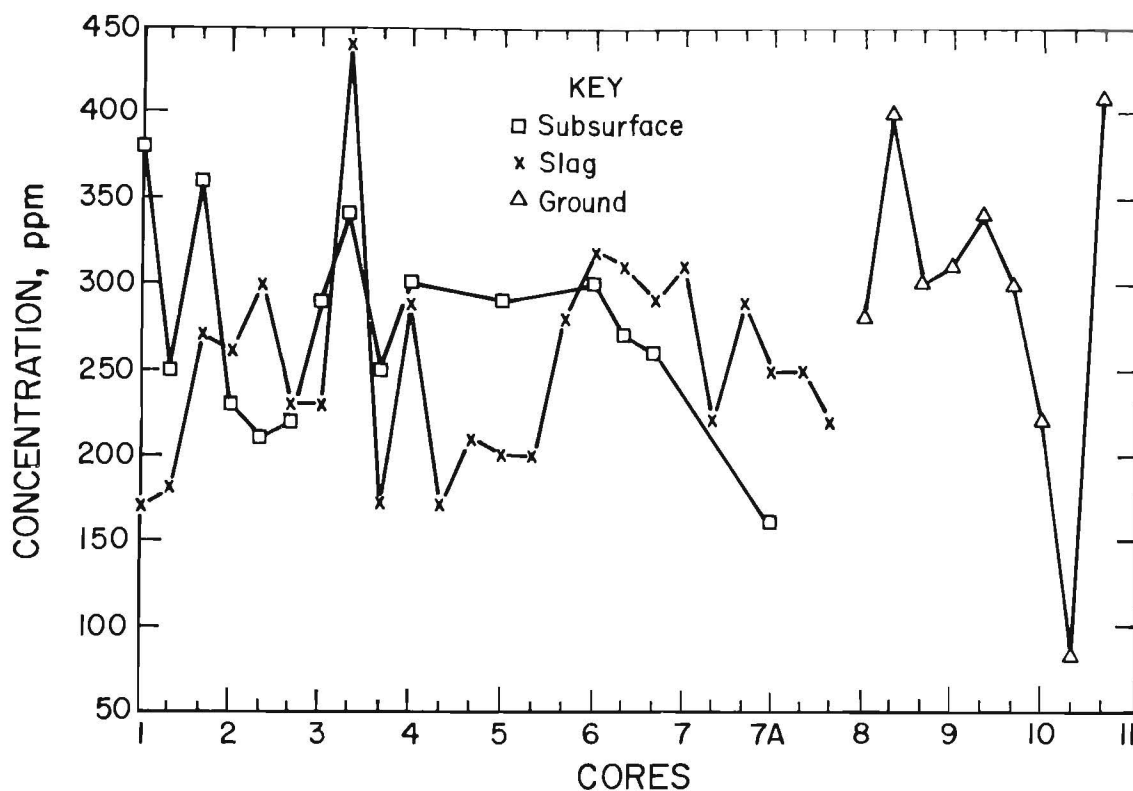
Figure 13.–Arsenic concentrations in slag, subsurface, and ground material.

FLUORIDE ANALYSES

The fluoride analyses given in table 5 are illustrated in figure 14. This figure shows that there are considerable differences in the concentrations of fluoride in the slag samples compared with that in the subsurface or ground samples. Tables 10 and 11 summarize these data.

The slag-subsurface probability shows that there is a definite difference between the fluoride concentration in the slag and in the subsurface material, also illustrated in figure 14. The probabilities also indicate that the east and the west slag stockpiles are different; and that the subsurface and the ground concentrations are different. The slag concentration was 3.87 pct; the subsurface, 0.18 pct; and the ground, 0.08 pct. This indicates that some leaching of fluoride from the slag to the subsurface may occur.

Table 10.–Average concentrations of fluoride, percent

Samples	Analyses	Conc	Std dev
Slag[1]	24	3.87	0.45
East slag	9	4.14	.40
West slag	15	3.76	.36
Subsurface	15	.18	.16
Ground	9	.08	.03

[1]East and west slag samples.

Table 11.–Statistical comparison of fluoride analyses

Comparison	t-test value	Probability
Slag-subsurface	30.222	0.0000
East-west slag	2.337	.0289
Subsurface-ground . .	1.909	.0694
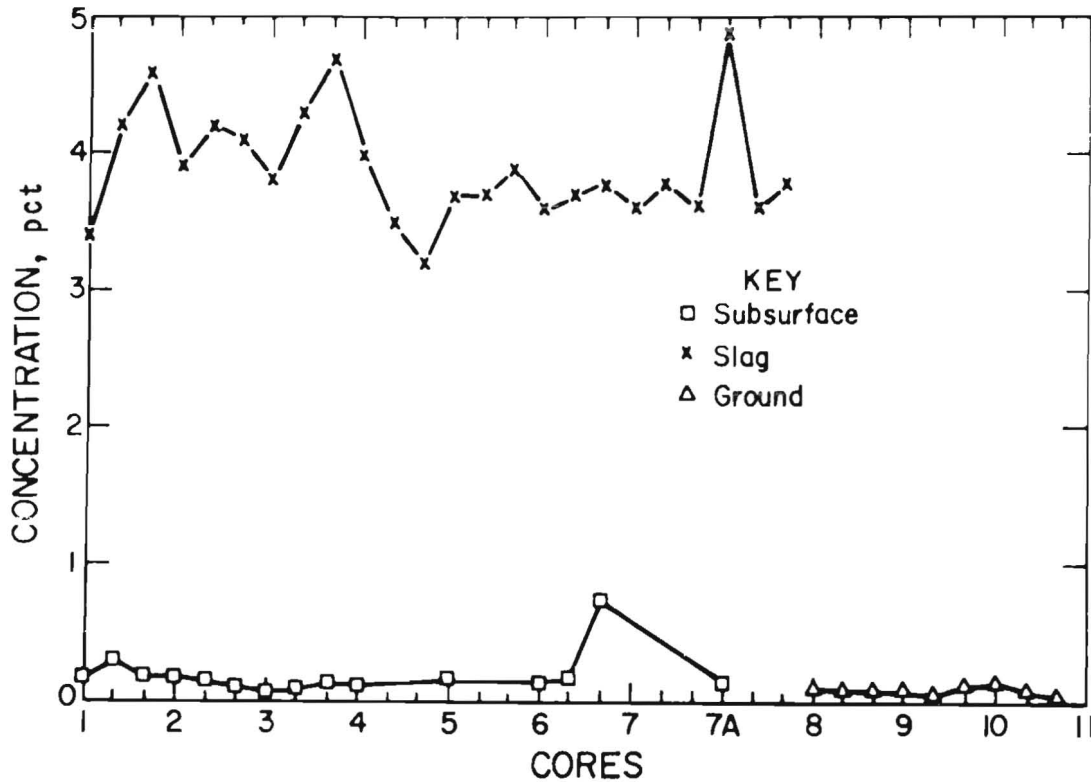
Figure 14.–Fluoride concentrations in slag, subsurface, and ground material.

RADIUM-226 ANALYSES

The Ra^{226} analyses given in table 6 are illustrated in figure 15. This figure shows that there are considerable differences in the concentrations of Ra^{226} in the slag samples compared with that in the subsurface or ground samples. Tables 12 and 13 summarize these data.

The slag-subsurface probability shows that there is a definite difference between the Ra^{226} concentration in the slag and in the subsurface material, as shown in figure 15. The probabilities indicate that the concentrations of Ra^{226} in the east and west slags are statistically the same, and that the concentrations of Ra^{226} in the subsurface and ground are statistically the same. The slags do not affect the subsurface, and the subsurface Ra^{226} concentration and that of the ground are below the limit of 5 pCi/g set by EPA (13).

These results indicate that Ra^{226} is not leached from the slag material and does not contaminate the surrounding area or the ground water.

Table 12.–Average concentrations of
Radium-226, picocuries per gram

Samples	Analyses	Conc	Std dev
Slag[1]	7	28.67	5.30
East slag	3	28.81	7.76
West slag	4	28.57	4.01
Subsurface	6	2.13	.86
Ground	3	1.88	.48

[1]East and west slag samples.

Table 13.–Statistical comparison of
Radium-226 analyses

Comparison	t-test value	Probability
Slag-subsurface	12.059	0.0000
East-west slag	.054	.9959
Subsurface-ground . .	.447	.6682
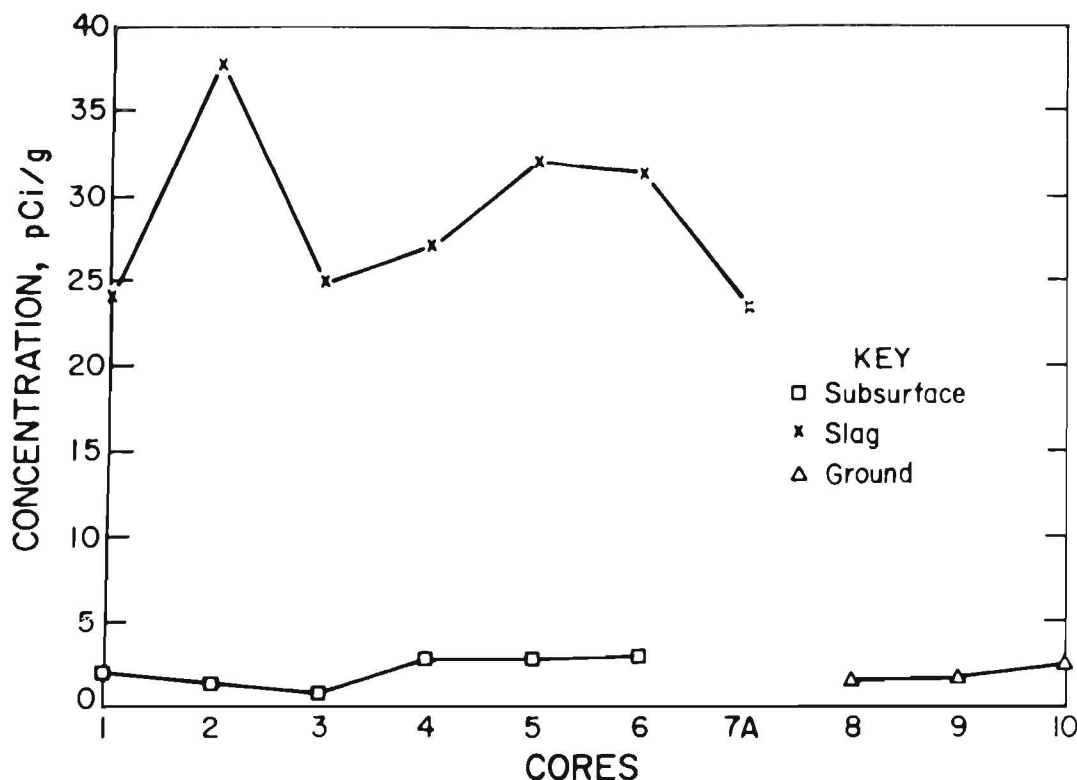
Figure 15.–Radium-226 concentrations in slag, subsurface, and ground material.

WATER ANALYSES

The concentrations of all elements (table A-5) are equal to or greater in the seepage water (sample 2W) than in the depression pond on the slag pile (sample 1W). The concentrations of Na, Mg, Ca, Sr, Ba, Cr, Mn, Co, Cu, Cd, Al, and P are greater in the seepage water than in the Pond Creek water samples (samples 3W, 4W, and 5W) and indicates that these elements are leached from the slag piles.

The seepage water (table 7) from the east slag stockpile (sample 2W) increases in acidity, hardness, total sulfates, and in the elements Ba, Cd, Cr, and Hg from that of the pond water (sample 1W) on the east slag stockpile. All of these concentrations decrease as soon as the seepage water reaches the Pond Creek water (sample 4W) at the slag stockpile. Seepage water from an industrial waste stockpile would not usually be considered as drinking water, and the seepage from the phosphate slag stockpile exceeded the drinking water standards for Cr, Hg, and fluoride. The Cr and fluoride concentrations are reduced to an acceptable level by the time the seepage water reaches the Pond Creek water (sample 4W); and downstream from the slag (sample 5W), the Hg level is also reduced to below drinking water standards, and seepage from the slag stockpile has not contaminated this water.

EPA EXTRACTION PROCEDURE TOXICITY TESTS

All samples (table 8) are below the EPA requirements for the characteristic of EPA toxicity. The EPA EP toxicity test of the east slag pile (table 8, sample 1C) and the analysis of the water seepage (table 7, sample 2W) should be a measure of the same thing–the concentrations of toxic elements leached from the slag under acidic conditions. Results from the EPA EP toxicity test yielded concentrations 2 to 200 times greater than those of the seepage water analyses.

The east slag stockpile had a unique situation: a depression on top of the stockpile containing rain water, a permeable slag material that allowed water to freely seep through the material, an impermeable base subsurface material, and a seepage drainage that allowed collection of water that had passed through the slag material. These conditions were ideal for determining elements naturally leached from the stockpile by analyzing the water before and after its passage through the stockpile.

Any laboratory EP toxicity test should imitate the normal conditions at a stockpile and produce the same results. The EPA EP toxicity test may not be applicable to the slag stockpiles investigated, since the EPA results predicted a much larger extraction of toxic elements than actually occurred.

SOURCE OF ELEMENTS IN SLAG

Phosphate rock, sand, and coke were used in the production of elemental phosphorus. These raw materials were the source of elements in the slag, with the exception of those elements removed during the production of phosphorus, such as the phosphorus itself, those washed from the slag by rain, those added by windblown dust, or those introduced by waste management practices at the site. A comparison of toxic elements, fluoride, Ra^{226}, K, and Na concentrations in the slag with those in the phosphate rock may be informative. Table 14 contains analyses of the slag from this report and analyses of typical phosphate rock (3, 14).

Although the phosphate rock reported in the literature may differ somewhat from that used in producing the slag, comparisons of concentrations indicate that As, Ba, Pb, Ag, K, and Na may have a source other than the byproduct of the elemental phosphorus production.

Table 14.-Analyses of slag[1] and typical phosphate rock

		Slag	Phosphate rock		Conc ratios[2]
			Literature value	References	
Ag	ppm ..	18.5	5	3	3.7
As	ppm ..	252.5	20	3	12.6
Ba	ppm ..	487.9	70	3	7.0
Cd	ppm ..	1.6	30	3	0.1
Cr	ppm ..	72.6	100	3	0.7
Hg	ppm ..	[3]1.2	7	3	0.2
K	pct ..	0.7	0.1	14	7.0
Na	pct ..	1.2	0.4	14	3.0
Pb	ppm ..	99.0	50	3	2.0
Ra	pCi/g ..	28.7	38	3	0.8
Se	ppm ..	[3]0.4	7	3	0.1
Fluoride	pct ..	3.9	3.8	14	1.0

[1]This report.
[2]This report divided by literature value.
[3]Taken as 20 times EPA extraction value, since a 20:1 dilution is used in the procedure and no Hg or Se determinations were made directly on the slag.

SUMMARY

1. The phosphate slag is predominately $CaSiO_3$, and the subsurface material is clay and quartz.

2. The permeability of the slag material was 1.65×10^{-3} cm/s and that of the subsurface was 3.24×10^{-6} cm/s. Water leaching from the slag stockpiles would not, for all practical purposes, penetrate into the subsurface material, but would seep out through the slag into the drainage basin leading to the Tennessee River.

3. The average Ra^{226} concentration in the slag was 28.7 pCi/g, with a standard deviation of 5.3 pCi/g; concentration in the subsurface material was 2.1 pCi/g. Concentrations of Ra^{226} in the east and west slag stockpiles were the same; concentrations in the subsurface and the background were the same, indicating no leaching of Ra from the slag stockpiles.

4. The average fluoride concentration in the slag was 3.87 pct, with a standard deviation of 0.45 pct. The concentration in the east slag stockpile was greater than that in the west slag stockpile. The subsurface concentration was 0.18 pct and the background concentration was 0.08 pct.

5. Four elements—Mn, Co, Cu, and F—had higher concentrations in the subsurface than they did in the background.

6. Thirty elements—Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cr, Fe, La, Pb, Li, Mg, Mo, Ni, Nb, P, K, Ra, Ag, Na, Sr, Sn, Ti, W, V, Y, Zn, and Zr—had the same concentrations in the subsurface as they did in the background. This indicated that these elements were not leached from the slag into the subsurface material.

7. Seven elements—Li, K, Nb, Mo, Cu, As, and Sb—had the same concentrations in the slag as they did in the subsurface material. All other elements differ in their concentrations, as would be expected since the slag and the subsurface material are two different materials.

8. Six elements—Li, Na, Be, Ba, Pb, and F—had higher concentrations in the east than in the west slag stockpiles, and two elements—Fe and Al—had higher concentrations in the west stockpile.

9. Twelve elements—Li, Be, Sr, Cr, Mo, Fe, Ni, Cu, Zn, Al, Sn, and Sb—had higher concentrations in the top samples than in the bottom samples, while three elements—Be, Zn, and Sn—had higher concentrations in the bottom samples.

10. The slag stockpile material is not hazardous waste according to the EPA EP toxicity test.

11. Twelve elements—Na, Mg, Ca, Sr, Ba, Cr, Mn, Co, Cu, Cd, Al, and P—had higher concentrations in seepage water from the slag than in east slag stockpile pond or in water in Pond Creek. This indicates that these elements were leached from the slag piles. Analysis of the seepage water from the east slag stockpile gave lower concentrations of toxic elements than the EPA EP run on the slag from the east stack, indicating that the EP toxicity test may be inappropriate for mining and minerals processing wastes.

12. Concentrations of As, Ba, Pb, Ag, and K in the phosphate slag material indicate that some source other than the phosphate ore may be responsible for these elements in the stockpiles.

CONCLUSIONS

The phosphate slag stockpiles at TVA's NFDC, Muscle Shoals, AL, are not hazardous materials according to the EPA EP toxicity test. The Ra-226 concentration in the slag was 28.7 pCi/g, and that in the background material was 2.1 pCi/g. Evidence indicates that no Ra was leached from the slag into the ground. The fluoride concentration in the slag was 3.87 pct; in the subsurface material under the slag, 0.18 pct; and in the background material, 0.08 pct, indicating some mobility of fluoride.

The permeability of the slag material was 1.65×10^{-3} cm/s, and that of the subsurface material was 3.24×10^{-6} cm/s. Rain water, trapped in a depression on top of the east slag stockpile, became seepage water at the base of the stockpile, with a pH of 3.7. The concentrations of EPA toxic elements in the seepage water were much less than the concentrations of these elements in the EPA EP toxicity test.

Twelve elements—Na, Mg, Ca, Sr, Ba, Cr, Mn, Co, Cu, Cd, Al, and P—had higher concentrations in seepage water from the slag stockpiles than in water on top of the slag stockpiles, or in creek water adjacent to the base of the stockpiles, indicating that these elements were leached from the slag stockpiles. However, these leached elements did not contaminate the underlying aquifers because of the low permeability of the subsurface material.

REFERENCES

1. Moldovan, I., N. Popovice, and G. Chivu. The Technology of Mineral Fertilizers. Meridiane Publ. House, Bucharest, Romania, 1969, pp. 39-40, 214-219, 390-394.

2. May, A., and J. W. Sweeney. Assessment of Environmental Impacts Associated With Phosphogypsum in Florida. BuMines RI 8639, 1982, 19 pp.

3. _____. Evaluation of Radium and Toxic Element Leaching Characteristics of Florida Phosphogypsum Stockpiles. BuMines RI 8776, 1983, 18 pp.

4. Harris, H. B., G. K. Moore, and L. R. West. Geology and Groundwater Resources of Colbert County, Alabama. Geol. Surv. AL, Tuscaloosa, AL, County Report 10, 1963, 71 pp.

5. Knight, A. L., D. M. O'Rear, and J. R. Harkins. Surface Water Availability, Colbert County, Alabama. Geol. Surv. AL, Tuscaloosa, AL, Map 109, 1972, 10 pp.

6. Wendzel, L. K. Methods of Determining the Permeability of Water-Bearing Materials. U.S. Geol. Surv. Water-Supply Paper 887, 1942, pp. 50-87.

7. Ferris, J. G., D. B. Knowles, R. H. Brown, and R. W. Stallman. Theory of Aquifer Tests. U.S. Geol. Surv. Water-Supply Paper 1536-E, 1962, 173 pp.

8. U.S. Code of Federal Regulations. Title 40–Protection of Environment; Chapter I–Environmental Protection Agency; Subchapter D–Water Programs; Part 141–National Primary Drinking Water Regulations; Subpart B–Maximum Contaminant Levels; Section 141.11 Maximum Contaminant Levels for Inorganic Chemicals, July 1, 1986.

9. U.S. Code of Federal Regulations. Title 40–Protection of Environment; Chapter I– Environmental Protection Agency; Part 261–Identification and Listing of Hazardous Waste; Subpart D.–List of Hazardous Waste; Appendix II–EP Toxicity Test Procedures, July 1, 1986.

10. _____. Title 40–Protection of Environment; Chapter I– Environmental Protection Agency; Subchapter I–Solid Wastes; Part 261–Identification and Listing of Hazardous Waste; Subpart C– Characteristics of Hazardous Waste; Section 261.24–Characteristic of EP Toxicity, July 1, 1986.

11. U.S. Environmental Protection Agency. Test Methods for Evaluating Solid Waste. V. II: Field Manual, Physical/Chemical Methods, SW-846, 3d ed., ch. 9, sec. 9.1.1.1, Nov. 1986, p. 9-6.

12. Snedecor, G. W., and W. G. Cockran. Statistical Methods. IA State Univ. Press, Ames, IA, 6th ed., 1967, pp. 102-108.

13. U.S. Code of Federal Regulations. Title 40–Protection of Environment; Chapter I–Environmental Protection Agency; Subchapter F–Radiation Protection Programs; Part 192–Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings; Subpart D–Standards for Management of Uranium Byproduct Materials Pursuant to Section 84 of the Atomic Energy Act of 1954, as Amended; Section 192.33–Corrective Action Programs, July 1, 1986.

14. The Association of Florida Phosphate Chemists (Bartow, FL). Certificate of Analysis, AFPC Standard Check Sample No. 20, Florida Phosphate Rock. Nov. 2, 1979, 1 p.

APPENDIX A.–MOISTURE CONTENTS AND SPECTROGRAPHIC ANALYSES

Table A-1.–Moisture contents of core samples, percent

Core	Top	Middle	Bottom	Core	Top	Middle	Bottom	Core	Top	Middle	Bottom
EAST STOCKPILE				WEST STOCKPILE				GROUND[3]			
Slag:[1]				Slag:				8	18.0	26.3	28.9
1	7.3	5.0	6.6	4	5.5	4.4	6.1	9	17.2	27.2	23.8
2	11.6	12.5	12.0	5	4.4	5.0	5.0	10	17.4	21.3	30.0
3	4.8	7.1	6.7	6	4.2	6.4	5.3	Composite[4]	NS	23.8	NS
Subsurface:[2]				7	4.3	5.3	6.4				
1	20.2	22.8	23.6	7A	8.2	3.9	5.0				
2	25.4	21.6	21.4	Subsurface:							
3	15.6	18.1	21.9	4	20.7	NS	NS				
				5	19.2	NS	NS				
				6	22.7	23.3	20.7				
				7	NS	NS	NS				
				7A	19.5	NS	NS				

NS   No sample obtained.
[1]24 samples, 6.4 pct av moisture, 2.4 pct std dev.
[2]15 samples, 21.1 pct av moisture, 2.4 pct std dev.
[3]9 samples, 23.3 pct av moisture, 3.1 pct std dev.
[4]Samples 8, 9, and 10.

**Table A-2.–Spectrographic analyses–average concentrations of elements in slag,
subsurface and ground material samples**

(24 slag samples, 15 subsurface samples, 9 ground samples)

	Concentration			Std dev		
	Slag	Subsurface	Ground	Slag	Subsurface	Ground
Ag . . . . ppm . .	18.5	5.0	1.3	13.00	11.79	4.00
Al . . . . pct . .	4.1	5.5	7.0	0.25	1.30	2.82
As . . . . ppm . .	252.5	274.0	293.7	62.57	58.65	98.32
Ba . . . . ppm . .	487.9	154.3	150.9	84.08	40.76	48.60
Be . . . . ppm . .	1.6	<0.1	0.1	0.42	<0.10	0.22
Bi . . . . ppm . .	134.4	39.5	7.0	84.91	72.51	21.00
Ca . . . . pct . .	28.3	0.8	0.2	1.20	1.34	0.34
Cd . . . . ppm . .	1.6	3.6	2.2	3.53	2.28	1.23
Co . . . . ppm . .	12.0	30.0	15.0	6.18	10.56	9.77
Cr . . . . ppm . .	72.6	126.1	130.3	25.85	32.54	50.10
Cu . . . . ppm . .	41.4	38.5	28.1	11.52	12.35	10.18
Fe . . . . pct . .	1.0	3.2	3.9	0.29	0.60	1.68
K . . . . pct . .	0.7	0.7	0.6	0.06	0.18	0.26
La . . . . ppm . .	157.9	95.9	83.4	51.67	28.23	44.42
Li . . . . ppm . .	48.6	40.6	37.7	37.06	10.15	13.49
Mg . . . . pct . .	0.4	0.2	0.2	0.07	0.06	0.09
Mn . . . . ppm . .	687.9	1,000.7	493.3	129.78	637.52	400.81
Mo . . . . ppm . .	25.0	23.1	21.2	8.63	11.92	11.92
Na . . . . pct . .	1.2	0.1	0.1	0.50	0.02	0.03
Nb . . . . ppm . .	17.4	24.2	21.5	18.72	13.85	8.28
Ni . . . . ppm . .	28.2	67.2	64.2	10.88	19.49	34.36
P . . . . pct . .	0.8	0.1	0.1	0.32	0.03	0.04
Pb . . . . ppm . .	99.0	59.0	53.7	45.65	29.92	27.43
Sb . . . . ppm . .	10.5	5.9	<0.1	40.22	22.72	0.08
Sn . . . . ppm . .	31.4	17.5	11.6	16.28	13.78	10.36
Sr . . . . ppm . .	527.5	112.5	92.7	28.78	28.97	54.21
Ti . . . . pct . .	0.1	0.3	0.4	0.02	0.08	0.15
V . . . . ppm . .	8.0	108.3	137.8	13.58	33.61	74.63
W . . . . ppm . .	115.0	81.9	86.2	37.63	36.25	44.92
Y . . . . ppm . .	157.5	104.7	126.3	38.02	62.21	146.39
Zn . . . . ppm . .	151.5	309.3	307.8	82.77	77.04	166.34
Zr . . . . ppm . .	236.3	109.0	127.2	30.05	29.26	56.85

Table A-3.–Spectrographic analyses–average concentrations of elements in east, west, top, middle, and bottom slag samples

(9 samples, east pile; 15 samples, west pile; 8 samples each, top, middle, and bottom)

	Concentration					Std dev				
	East	West	Top	Middle	Bottom	East	West	Top	Middle	Bottom
Ag .... ppm ..	22.2	16.3	16.0	23.6	16.0	20.64	4.51	6.23	21.27	4.50
Al .... pct ..	4.0	4.2	4.3	4.1	4.0	0.21	0.25	0.32	0.16	0.21
As .... ppm ..	250.0	254.0	253.8	258.8	245.0	84.85	48.08	52.63	89.67	44.08
Ba .... ppm ..	543.3	454.7	500.0	486.3	477.5	39.05	87.08	85.02	83.48	93.47
Be .... ppm ..	1.9	1.5	1.4	1.8	1.7	0.51	0.28	0.30	0.56	0.31
Bi .... ppm ..	159.4	119.4	113.4	166.9	123.0	135.75	25.89	37.96	139.51	30.44
Ca .... pct ..	29.6	27.5	28.1	28.3	28.3	0.39	0.69	1.47	1.22	1.04
Cd .... ppm ..	2.4	1.1	1.1	2.8	0.8	5.59	1.42	1.76	5.83	1.18
Co .... ppm ..	13.0	10.0	10.8	14.8	10.3	11.14	2.44	3.26	10.70	1.87
Cr .... ppm ..	73.3	72.2	72.5	80.4	65.0	31.83	10.35	18.71	40.55	8.09
Cu .... ppm ..	39.9	42.3	46.0	42.9	35.3	16.23	8.07	13.38	13.00	4.23
Fe .... pct ..	0.9	1.1	1.2	1.0	1.0	0.11	0.32	0.44	0.15	0.14
K .... pct ..	0.7	0.6	0.6	0.7	0.6	0.09	0.04	0.04	0.08	0.05
La .... ppm ..	147.8	164.0	143.8	188.8	141.3	44.94	55.91	28.75	29.06	18.85
Li .... ppm ..	66.9	37.7	62.8	42.1	41.0	57.41	5.45	60.24	18.68	13.83
Mg .... pct ..	0.4	0.4	0.4	0.4	0.4	0.10	0.05	0.07	0.09	0.07
Mn .... ppm ..	683.3	690.7	648.8	727.5	687.5	201.62	66.49	131.31	124.87	137.71
Mo .... ppm ..	26.9	23.9	24.9	28.1	22.0	13.54	3.72	4.61	13.89	2.98
Na .... pct ..	1.6	1.0	1.2	1.2	1.2	0.12	0.47	0.53	0.53	0.49
Nb .... ppm ..	22.2	14.5	14.0	24.6	13.7	29.86	6.51	8.53	30.78	6.59
Ni .... ppm ..	30.1	27.1	28.0	31.3	25.4	17.27	4.51	6.19	17.89	3.34
P .... pct ..	0.9	0.7	0.7	0.7	0.8	0.42	0.24	0.33	0.32	0.34
Pb .... ppm ..	131.1	79.8	95.4	111.3	90.5	40.14	38.02	45.47	59.13	31.87
Sb .... ppm ..	21.1	4.1	7.6	23.8	<0.1	63.33	15.75	21.57	67.18	0.00
Sn .... ppm ..	35.9	28.7	24.4	37.4	32.5	25.07	7.49	8.67	25.64	6.35
Sr .... ppm ..	523.3	530.0	551.3	515.0	516.3	31.62	27.77	24.75	25.63	22.00
Ti .... pct ..	0.1	0.1	0.1	0.1	0.1	0.01	0.01	0.02	0.02	0.02
V .... ppm ..	11.4	5.9	6.6	12.5	4.8	20.71	6.72	7.41	21.67	6.61
W .... ppm ..	125.3	108.7	110.0	128.8	106.1	59.91	12.82	16.69	61.51	15.99
Y .... ppm ..	144.4	165.3	147.5	173.8	151.3	15.09	45.49	25.49	58.05	16.42
Zn .... ppm ..	142.4	156.9	123.1	163.8	167.5	60.51	95.29	48.93	95.27	98.26
Zr .... ppm ..	226.7	242.0	228.8	245.0	235.0	14.14	35.70	35.57	33.81	23.30

Table A-4.–Spectrographic analyses–concentrations of elements in top ground samples

	8	9	10				8	9	10
Ag .... ppm ..	<10.00	<10.00	<10.00	Mn	ppm ..		290.00	220.00	570.00
Al .... pct ..	6.70	7.00	5.30	Mo	ppm ..		15.00	13.00	36.00
As .... ppm ..	280.00	310.00	220.00	Na	pct		0.04	0.02	0.03
Ba .... ppm ..	140.00	120.00	170.00	Nb	ppm ..		22.00	20.00	18.00
Be .... ppm ..	<0.20	<0.20	<0.20	Ni	ppm ..		33.00	33.00	62.00
Bi .... ppm ..	<60.00	<60.00	<60.00	P	pct		0.14	0.05	0.05
Ca .... pct ..	1.10	0.15	0.07	Pb	ppm ..		50.00	40.00	44.00
Cd .... ppm ..	1.00	1.10	1.00	Sb	ppm ..		<60.00	<60.00	<60.00
Co .... ppm ..	10.00	6.90	26.00	Sn	ppm ..		8.10	4.70	15.00
Cr .... ppm ..	87.00	120.00	110.00	Sr	ppm ..		32.00	32.00	84.00
Cu .... ppm ..	22.00	18.00	33.00	Ti	pct		0.46	0.46	0.24
Fe .... pct ..	3.40	4.30	2.90	V	ppm ..		90.00	110.00	120.00
K .... pct ..	0.40	0.36	0.81	W	ppm ..		76.00	79.00	68.00
La .... ppm ..	41.00	42.00	66.00	Y	ppm ..		17.00	14.00	110.00
Li .... ppm ..	36.00	31.00	38.00	Zn	ppm ..		140.00	110.00	300.00
Mg .... pct ..	0.21	0.17	0.29	Zr	ppm ..		170.00	170.00	95.00

Note.–Core 8, east of stockpiles; core 9, between stockpiles; core 10, west of stockpiles.

Table A-5.–Spectrographic analyses of water samples, parts per million

	1W	2W	3W	4W	5W		1W	2W	3W	4W	5W
Ag	<0.05	<0.05	<0.05	<0.05	<0.05	Mn	.11	16.00	<.01	.04	<.01
Al	8.70	9.70	<.30	<.30	<.30	Mo	<.05	<.05	<.05	<.05	<.05
As	<.30	<.30	<.30	<.30	<.30	Na	3.70	51.00	33.00	31.00	31.00
Ba	<.01	.17	.02	.03	.04	Nb	<.02	.03	<.02	<.02	<.02
Be	<.01	<.01	<.01	<.01	<.01	Ni	<.03	<.07	<.03	<.03	<.03
Bi	<.30	<.30	<.30	<.30	<.30	P	<1.00	1.60	<1.00	<1.00	<1.00
Ca	13.00	120.00	22.00	23.00	14.00	Pb	<.10	.10	<.10	<.10	<.10
Cd	<.01	<.01	<.01	<.01	<.01	Sb	.30	.30	.30	.30	.30
Co	.01	.26	.01	.01	.01	Sr	.01	.23	.04	.04	.03
Cr	<.04	.06	<.04	<.04	<.04	Sn	<.02	.04	.06	.06	.08
Cu	.25	.60	.14	.53	<.06	Ti	<.03	<.03	<.03	<.03	<.03
Fe	<.05	<.05	<.05	<.05	<.05	V	<.05	<.05	<.05	<.05	<.05
K	11.00	41.00	57.00	22.00	21.00	W	<.30	<.30	<.30	<.30	<.42
La	<.04	<.04	<.04	<.04	<.04	Y	<.01	<.02	<.01	<.01	<.01
Li	<.03	<.03	<.03	<.03	.03	Zn	<.03	.28	<.03	.25	.07
Mg	2.80	12.00	4.70	4.90	4.60	Zr	<.10	<.10	<.10	<.10	<.10

1W Depression pond in east slag stockpile.
2W Seepage from east slag stockpile.
3W Pond Creek, upstream from east slag stockpile.
4W Pond Creek, at east slag stockpile.
5W Pond Creek, downstream from east slag stockpile.

APPENDIX B.–PERMEABILITY

The permeability results, shown in table 4, were treated as follows: D'Arcy's law for the flow of water through soil (6)[1] is

$$V/t = P(A)(h/L), \qquad (B-1)$$

where   V = volume of water,

   t = time,

   P = permeability,

   A = area,

   h = hydraulic head,

and   L = length of water path.

Rearranging equation B-1 and integrating with respect to t and h gives

$$\ln h = C/V + [(P/L)(A/V)](t) = a - bt, \quad (B-2)$$

where   C = integration constant,

and   a, b = coefficients in the linear equation that are determined from the data.

The minus sign in the right hand expression, equation B-2, is due to the data treatment, with the levels of water decreasing during the permeability measurements. The data were fitted by least squares linear regression to equation B-2, yielding the results for slag and subsurface material, respectively: correlation coefficient (r), -0.998 and -0.992; a, 3.783 and 3.802; and b, -7.008 x 10^{-5} and -1.331 x 10^{-7}. The correlation coefficients indicate excellent fits of the data to equation B-2. The permeability, P, is given the equation

$$P = -b(L)(V/A)/t . \qquad (B-3)$$

The term (V/A) equals a length, so equation B-3 yielded the following permeability values for slag and subsurface material, respectively: 1.65 x 10^{-3} cm/s (2.34 in/h) and 3.27 x 10^{-6} cm/s (4.59 x 10^{-3} in/h).

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[1]Italic numbers in parentheses refer to items in the list of references preceding appendix A.